

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN OR RELATING TO THE PRODUCTION OF ALKYLENE GLYCOL ESTERS

(71) We, MITSUBISHI CHEMICAL INDUSTRIES LIMITED, a company organised according to the laws of Japan, of 5—2, Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for producing alkylene glycol esters, e.g., ethylene glycol esters, involving the oxidative acylation of olefines.

Alkylene glycol esters are useful as solvents and plasticizers. For example, ethylene glycol esters may be used as a solvent, or as an intermediate in the manufacture of ethylene glycol which is a commercially significant intermediate in the production of polyethylene terephthalate.

A variety of catalysts are known to be useful for the production of alkylene glycol esters by the reaction of olefines, carboxylic acids and molecular oxygen.

U.S. Patent Specification No. 3,770,813 to Kollar, issued Nov. 6, 1973, discloses a process employing a catalyst system consisting of iodine (or an iodine-producing compound and oxygen) and at least one cation selected from alkali metal cations, a heavy metal cation of atomic number 21—30 and 48, and nitrogen-containing cations derived from tri-lower alkyl amines, ammonia, piperidine or pyridine. The drawback of this process is relatively low reaction rates which require the use of high reaction temperatures in a range of 130 to 160°C, and relatively higher reaction pressures.

U.S. Patent Specification No. 3,689,535 to Kollar, issued Sept. 5, 1972, discloses a process which involves the use of a catalyst system consisting of bromine or chlorine (or a bromine or chlorine-containing compound) and a variable valency metal cation such as Ce, Mn, Sb, V, Ga, As, Cr, Cu, Ag and Co. This process suffers from relatively low reaction rates which require the use of high reaction temperatures in a range of 80 to 200°C. A further disadvantage of this process is the corrosion problem associated with the corrosive nature of this catalyst system at high temperatures. U.S. Patent Specification No. 2,519,754 to Gresham *et al*, issued Aug. 22, 1950, discloses the use of hydrogen halides (preferably hydrobromic acid) or organic halides (preferably aliphatic bromides) as a catalyst. However, this process requires the use of high reaction temperatures in a range of 180°C to 220°C.

U.S. Patent Specification No. 3,427,348 to Olson, issued Feb. 11, 1969, discloses a catalyst system consisting of selenium dioxide and a mineral acid. The disadvantage of this catalyst system is relatively low selectivity.

U.S. Patent Specification No. 3,778,468 to Kollar, issued Dec. 11, 1973, discloses a process for the production of ethylene glycol esters employing a catalyst comprising

cationic selenium and at least one halogen or halogenated substance selected from the bromine, chlorine, a bromine-producing compound and a chloride-producing compound.

U.S. Patent Specification No. 3,668,239 to Kollar, issued June 6, 1972, discloses a catalyst system consisting of tellurium and an appropriate bromine source.

U.S. Patent Specification No. 3,479,395 to Huguet, issued Nov. 18, 1969, discloses a catalyst system consisting of tellurium dioxide, an alkali metal halide and a redox system.

U.S. Patent Specification No. 2,497,408 to Gresham, issued Feb. 14, 1950, discloses a process for the manufacture of propylene glycol esters employing a mixed catalyst of a metal acetate such as lead acetate or ferric acetate and an alkaline earth metal acetate.

U.S. Patent Specification No. 3,299,110 to Pine, issued Jan. 17, 1967, discloses a molybdenum-containing catalyst such as molybdenum sulphide, molybdenum oxide and sulphided cobalt molybdate.

British Patent Specification No. 1,058,995 discloses a catalyst system consisting of palladium II salt, metal acetate such as alkali metal, alkaline earth metal, cupric, ferric, stannic and nickel acetates, and a metal halide selected from alkali metal, alkaline earth metal, cupric, ferric, stannic and nickel chlorides and bromides.

British Patent Specification No. 1,124,862 discloses a catalyst system consisting of a palladous salt and a nitrogen oxide-containing compound such as a nitrate or nitrite of a metal of Group I, II or VIII of the Periodic Table, nitric acid, nitrous acid, NO, NO₂, N₂O₃ or N₂O₅.

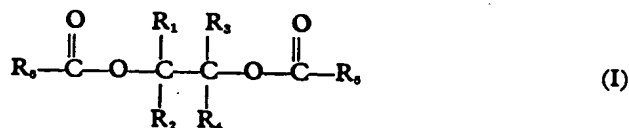
U.S. Patent Specification No. 3,262,969 to Clark *et al.*, issued July 26, 1966, discloses a catalyst system consisting of a palladous salt, a salt of a carboxylic acid, an alkali metal halide and a redox system.

U.S. Patent Specification No. 3,349,118 to Kohll *et al.*, issued Oct. 24, 1967, discloses a catalyst system consisting of palladium acetate and nitric acid. However, the processes employing a palladium salt as a main catalyst pose the disadvantages such as a loss of expensive palladium salts during the operation, plugging of the system caused by the deposit of palladium metal, and relatively low selectivity caused by the formation of unwanted by-products such as aldehydes and ketones.

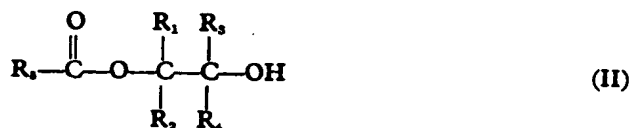
There is a need, therefore, for a more efficient, selective and inexpensive process for the production of alkylene glycol esters from olefines and carboxylic acids.

Accordingly, it is an object of this invention to provide a commercially practical process for producing alkylene glycol esters in high yields.

According to the present invention there is provided a process for the production of an alkylene glycol ester having the general formula (I):



wherein R₁, R₂, R₃ and R₄ are selected from hydrogen, C₁—C₂₀ alkyl and C₆—C₂₀ aryl, and R₅ is C₁—C₂₀ alkyl or C₆—C₂₀ aryl, and/or an alkylene glycol ester having the general formula (II):



wherein R₁, R₂, R₃, R₄ and R₅ are as defined herein above, any of the above-mentioned alkyl and aryl groups being optionally substituted, which comprises reacting in a liquid phase an olefine having the general formula (III):

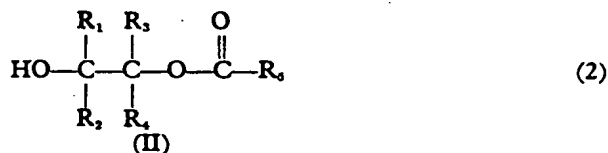
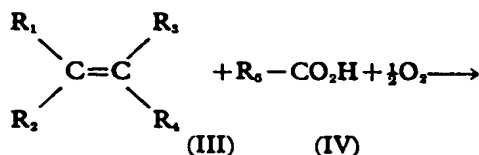
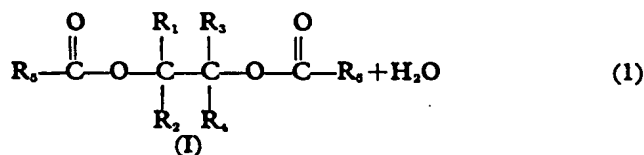
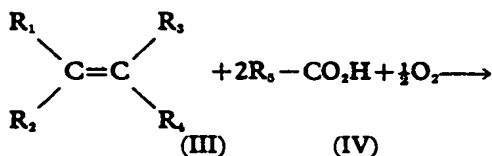


wherein R_1 , R_2 , R_3 and R_4 are as defined herein above, a carboxylic acid having the formula (IV):



wherein R_5 is as defined herein above, and molecular oxygen or other oxidising agent, in the presence of iodine or an iodine-containing compound which can reversibly vary its oxidation number and a nitrogen oxide or a compound containing a nitrogen oxide which can reversibly vary its oxidation number as catalyst.

The method of this invention is illustrated by the following chemical equations:



In the above formulae, R_1 , R_2 , R_3 and R_4 are selected from hydrogen, alkyl of 1—20 (preferably 1—10) carbon atoms and aryl of 6—20 (preferably 6—10) carbon atoms, and R_5 is alkyl of 1—20 (preferably 1—10) carbon atoms or aryl of 6—20 (preferably 6—10) carbon atoms. The above-described alkyl or aryl may be substituted with reaction-inert substituents such as halo, nitro, alkoxy, alkoxycarbonyl and carbonyl.

Suitable olefines (III) for use in the present process include straight-chain olefines such as ethylene, propylene, 1-butene, 2-butene, 1-hexene, 1-octene and 1-decene; and branched-olefines such as isobutylene, 2-methyl-1-pentene and 2-methyl-1-butene. Preferred olefines are ethylene and propylene.

Suitable carboxylic acids (IV) for use in the present process include aliphatic carboxylic acids such as acetic acid, monochloroacetic acid, propionic acid, butyric acid, valeric acid, isovaleric acid, octanoic acid, phenylacetic acid, and phenylpropionic acid, and aromatic carboxylic acids such as benzoic acid and toluic acid.

Preferred carboxylic acids are acetic acid, propionic acid and benzoic acid. Especially preferred is acetic acid. Preferably the reaction is carried out in the liquid phase. It is to be noted that when water is present in the reaction system in an amount sufficient to effect the hydrolysis of alkylene glycol diesters (I), alkylene glycol monoesters and alkylene glycols are obtained.

It is also to be noted that the presence of water favours the formation of alkylene glycols by the oxidative hydroxylation of olefines as well as by the hydrolysis of the alkylene glycol esters.

The characteristic feature of this invention is the use of a catalyst system comprising iodine or an iodine-containing compound and a nitrogen oxide or a compound containing a nitrogen oxide.

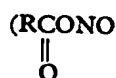
As used hereinabove, and as will be used hereinafter the term "a nitrogen oxide"

is intended to include oxides of nitrogen such as NO, N₂O, NO₂, N₂O₃, N₂O₄ and N₂O₅, and the term "a compound containing nitrogen oxide" is intended to include nitrogen-containing oxyacids such as nitrous acid, hyponitrous acid and nitric acid, and the salts of the oxyacids.

It is believed that iodine or an iodine-containing compound acts as a catalyst while reversibly varying its oxidation number, and the iodine or iodine-containing compound is believed to be present in the reaction system in the form of I⁻, I₂, I₂O, HIO, R—CO₂I (wherein R is optionally substituted alkyl), IO₃⁻ or I₂O₅. Therefore, iodine or any iodine-containing compound capable of affording in the reaction system a species of an iodine-containing compound which can reversibly vary its oxidation number may be introduced into the reaction system. Examples of such iodine-containing compounds are hydroiodic acid and salts thereof, such as lithium iodide, sodium iodide, potassium iodide, magnesium iodide and copper iodide; hypoiodous acid and salts thereof; iodic acid and the salts thereof; periodic acid and salts thereof; complex compounds of iodine; and organic iodine compounds, such as ethyl iodide and isopropyl iodide, which readily liberate iodide ion by solvolysis under reaction conditions.

The amount of the iodine or iodine-containing compound to be used is not critical, and is normally up to one equivalent per litre of the reaction solution.

It is also believed that a nitrogen oxide or a compound containing a nitrogen oxide which is another essential component of the catalyst system used in this invention acts as a catalyst, in a manner similar to that of the iodine or iodine-containing compound, while reversibly varying its oxidation number, and the nitrogen oxide is believed to be present in the reaction system in the forms of N₂O, NO, NO₂, N₂O₃, N₂O₄, N₂O₅, HNO₃, NO₂⁻, NO₃⁻ alkyl nitrites (R—ONO wherein R is optionally substituted alkyl), or optionally substituted alkyl carbonyl nitrites



wherein R is optionally substituted alkyl). Therefore, any nitrogen oxide or compound containing nitrogen oxide capable of affording in the reaction system a species of a nitrogen oxide which can reversibly vary its oxidation number may be introduced into the reaction system.

Examples of compounds containing nitrogen oxides are nitric acid and salts thereof such as alkali metal, alkaline earth metal and copper nitrates; nitrous acid and salts thereof such as alkali metal; alkaline earth metal and copper nitrites. Examples of nitrogen oxides are NO, NO₂, N₂O₃, N₂O₄ and N₂O₅. Mixtures of nitrogen oxide-containing compounds and/or nitrogen oxides may be used.

The amount of the nitrogen oxide to be used is not critical, and is generally up to one mole (calculated as nitrogen oxide) per litre of the reaction solution.

The process of this invention can be carried out by introducing into the reactor in addition to the above-described catalyst system a promoter selected from carbon and elements selected from lithium, beryllium, boron, sodium, magnesium, aluminium, silicon, potassium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, germanium, gallium, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, antimony, tellurium, barium, cerium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, mercury, thallium, lead and bismuth, and compounds containing any of the said elements.

The preferred promoters are carbon and elements selected from lithium, boron, sodium, aluminium, silicon, potassium, vanadium, iron, cobalt, nickel, copper, zinc, zirconium, molybdenum, tellurium, tungsten, platinum, gold, lead and bismuth and compounds containing any of the said elements.

Especially preferred are carbon and elements selected from boron, iron, cobalt, nickel, zirconium and platinum and compounds containing any of the said elements.

The addition of the promoter accelerates the reaction without lowering the selectivity of product obtainable.

The carbon which may be used is generally activated carbon including micro-crystalline carbon and graphite. There is no particular limitation on the raw material and the activation method of the carbon. There is no stringent limitation on the content of trace components and the crystal structure of the activated carbon, and therefore, commercially available activated carbon can be used. Likewise, there is no especially strict limitation on a preparation method and physical properties of the graphite.

There is no particular limitation on the shape of the graphite, and a powdery or granular graphite having a suitable particle size can be used.

The said elements may be added as such or in the form of compounds. There is no particular limitation on the form of the compounds, and they may be added in the form of oxides, sulphides, acids or bases which contains the above elements or salts. For example, platinum or platinum compounds having a valency of zero or more can be incorporated into the reaction system. Examples of such platinum or platinum compounds are platinum in the form of sponge, wire, powder crystal, foil or powder; platinum black; metallic platinum supported on a carrier such as activated carbon, carbon black, silica, alumina or asbestos; halogeno-platinic acids such as chloroplatinic acid, bromoplatinic acid and iodoplatinic acid; the salts of the halogenoplatinic acid; platinum halides such as platinum chloride, platinum bromide and platinum iodide; platinum salts of organic and inorganic acids such as platinum sulphate, platinum nitrate and platinum acetate; platinum oxides and sulphides; and complex compounds of platinum such as tetrammine-platinum dichloride and tetracyanoplatinic acid.

It is noteworthy that the results of the reaction are not quite affected by solubility or otherwise of the promoter.

The amount of the promoter which may be used varies widely with the reaction temperature, the nature of the promoter, the amount of the catalyst, etc. Advantageously, only small amounts of the promoter, e.g., 10^{-3} to 10^{-1} m mol per litre of the reaction solution, are needed for the successful operation of the process but larger amounts, e.g., up to one mole per litre of the reaction solution can also be used. The reaction mechanism for the process of this invention whereby alkylene glycol esters are obtained by the oxidative acylation of olefines is not fully understood. However, the following mechanism is possible.

Oxidation of a nitrogen oxide or a compound containing nitrogen oxide with an oxidizing agent, e.g., molecular oxygen converts the nitrogen oxide to its oxidized form which then oxidizes a reduced form of iodine or iodine-containing compound, e.g., iodide ion, being present in the system, to give its oxidized form, e.g., I_2 , I_2O , IO^- , IO_2^- , whereby the nitrogen oxide becomes reduced to its initial valency state. The oxidized form of the iodine or iodine-containing compound being formed, alone, or with the aid of a carboxylic acid, oxidizes an olefine to give an alkylene glycol ester, whereby the iodine or iodine-containing compound becomes reduced to its initial valency state. While repeating the above-described reaction as one cycle, the chain reaction proceeds.

It follows from the above that generally the only requirement for the nitrogen oxide or compound-containing nitrogen oxide and the iodine or iodine-containing compound used in the process of this invention is that they be capable of undergoing alternative oxidation and reduction under the reaction conditions.

Therefore, any nitrogen oxide or compound-containing nitrogen oxide and iodine or an iodine-containing compound each capable of undergoing alternative oxidation and reduction in the reaction system can be used regardless of their initial valency state.

The role of the promoter is not fully understood.

However, it is believed that the promoter accelerates the oxidation of the reduced forms of the nitrogen oxide or compound containing nitrogen oxide and the iodine or iodine-containing compound.

As stated above, the oxidizing agent employed in the process of this invention oxidizes the nitrogen oxide or compound containing nitrogen oxide from a lower valency state to a higher valency state. In general, molecular oxygen is used as an oxidizing agent.

However, in place of molecular, an oxidizing agent capable of oxidizing nitrogen oxides or compounds containing nitrogen oxides, such as hydrogen peroxide, organic peroxides, persulphates, bromine, chlorine, ozone or the like can be used. In order for the process of this invention to be economically advantageous, it is preferred to use molecular oxygen as an oxidizing agent. Oxygen may be introduced into the reaction mixture as a stream of the substantially pure gas. Alternatively, it may be introduced as air or as a mixture of oxygen with a gas inert to the reaction such as nitrogen.

In general, the reaction is carried out in the presence of a solvent. Examples of such solvents are the olefine starting materials, the carboxylic acid starting materials, the alkylene glycol ester products, glycols and a mixture thereof. Preferably, the carboxylic acid is used as a solvent as well as the source of the acid moiety of the desired ester.

In a continuous process, it is preferred that the glycol and its ester be separated from the reaction liquid, whereas the unreacted carboxylic acid and olefine be recovered for re-use.

If desired, organic or inorganic solvents which are substantially inert to the reaction may be used as a solvent or a portion of the solvent. For example, when the reaction is carried out employing ethylene as an olefine, acetic acid as a carboxylic acid and the same amount of water as that of acetic acid as a solvent, the reaction rate and the selectivity are nearly equal to those obtained when water is not added, and the main products are ethylene glycol monoacetate and ethylene glycol diacetate. When water is added in an amount larger than that of acetic acid, ethylene glycol is formed as a by-product. However, the formation of glycols is not a hindrance to commercial development of the process of this invention, because the glycols find wide uses.

The reaction temperature is not critical in the present invention except to retain a liquid phase. The lower the temperature, the lower is the reaction rate. On the other hand, the higher the temperature, the lower is the solubility of the gaseous starting materials (olefines, oxygen, iodine or iodine-containing compounds and nitrogen oxides or nitrogen oxide-containing compounds) in the reaction mixture.

The preferred reaction temperature is in a range of from room temperature to 200°C.

The reaction pressure is not an important variable and generally any pressure sufficient to maintain a liquid phase at the temperature being used is satisfactory. The reaction rate becomes higher as the reaction pressure increases. However, a high reaction pressure requires the use of a costly high pressure reactor. Accordingly, the preferred reaction pressure is generally in a range of from atmospheric pressure to about 50 kg/cm².

The reaction is carried out in any suitable apparatus, e.g., fixed bed, slurry-type and moving bed reactor, and can be done batchwise or continuously.

In general, the carboxylic acid is added in liquid form. In a continuous process, the unreacted carboxylic acid, after leaving the reactor, will be separated from the reaction mixture for re-use.

Gaseous olefine may be introduced alone or in combination with molecular oxygen into the reactor. Liquid or solid olefine may be introduced into the reactor alone or as a solution by dissolving it in a reaction medium, or as a gas by gasifying it in a vaporizer. The unreacted olefine, after leaving the reactor, may be separated from the reaction products for re-use.

The iodine or iodine-containing compound and the nitrogen oxide or nitrogen oxide-containing compound may be separated from the reaction products, and can be re-used after being subjected to a suitable operation for regeneration, e.g., reoxidation, if necessary.

A promoter which is completely dissolved in the reaction system can be recycled into the system along with the iodine or iodine-containing compound and the nitrogen oxide or nitrogen oxide containing compound. The promoter which may be suspended in the reaction system can be kept in the system by placing a filter at the liquid exit from the reactor, or can be recycled into the system by removing a portion of the reaction liquid from the reactor and then recovering it by filtration followed by being subjected to a suitable operation for regeneration, if necessary.

A promoter which is insoluble in the reaction system can be used as a fixed bed or fluidized system such as a slurry dispersion. Typical supports for fixed bed systems include kieselguhr, silicon carbide and titania.

Having generally described this invention, a more complete description will be given with reference to certain examples and reference examples which are provided herein for purposes of illustration only.

In the following examples and reference examples, the products, the conversion and the selectivity of reaction products were investigated by gas chromatographic analysis.

EXAMPLE 1

To a 100 ml round bottom flask fitted with an agitator, a reflux condenser, a gas inlet tube and a thermometer were added 2 g (15 millimoles) of lithium iodide, 0.69 g (10 millimoles) of lithium nitrate and 80 ml of acetic acid. The flask was set up in a bath maintained at 80°C. A gas mixture comprising oxygen, nitrogen and ethylene was fed in proportions by volume of 0.8 O₂/7.2 N₂/1.2 ethylene through the reaction mixture at a rate of 1.15 standard litres per hour with continuous stirring of the reaction mixture.

At the conclusion of the one hour reaction period, the conversion of ethylene was 50%. Analysis showed the formation of ethylene glycol monoacetate (hereinafter referred to as "EGMA") and ethylene glycol diacetate (hereinafter referred to as "EGDA") as the products. The combined yields of EGDA and EGMA based on the reacted ethylene were 95%. Small amounts of ethylidene diacetate (hereinafter referred

to as "EDA") and acetaldehyde (hereinafter referred to as ACH) were obtained as by-products. At the end of the 5 hours reaction period, the conversion of ethylene and the selectivity of the products were not varied.

EXAMPLE 2

Employing 1 ml of nitric acid in place of lithium nitrate, Example 1 was repeated. At the conclusion of the one hour reaction period, the conversion of ethylene was 30%. The combined yields of EGDA and EGMA based on the reacted ethylene was 95%.

EXAMPLE 3

To a reactor similar to that described in Example 1 were added 3.3 g (20 millimoles) of potassium iodide, 1 ml (10 millimoles) of nitric acid and 80 ml of acetic acid. The flask was set up in a bath maintained at 80°C. A gas mixture comprising by volume 8.5% of oxygen, 80% of nitrogen and 11.5% of ethylene was fed through the reaction mixture at a rate of 1.15 standard litres per hour with continuous stirring of the reaction mixture. At the conclusion of the one hour reaction period, the conversion of ethylene was 45%, and the combined selectivities of the reacted ethylene to EGDA, EGMA and 2-iodoethyl acetate (hereinafter referred to as "IEA") were 95%.

EXAMPLE 4

To a reactor similar to that described in Example 1 was added 2.7 g (20 millimoles) of lithium iodide and 80 ml of acetic acid. The flask was set up in an oil bath maintained at 80°C. A gas mixture comprising by volume 78% of nitrogen, 11.2% of oxygen, 9.8% of ethylene and 1.0% of nitrogen dioxide was fed through the reaction mixture at a rate of 1.9 standard litres per hour with stirring of the reaction mixture. The reaction between ethylene and oxygen occurred about 3.5 hours after initiating the introduction of the gas mixture, and was continued for 8 hours, at the end of which time the conversions per pass of ethylene and oxygen were 22% and 10% respectively.

The total amount of nitrogen dioxide which was fed into the reactor during the 8 hours reaction period was about 6.7 millimoles. The combined amounts of EGMA, EGDA and IEA which were formed in the 8 hours reaction period were 17 millimoles.

EXAMPLE 5

A 300 ml titanium-lined autoclave, fitted with a stirring apparatus, a gas inlet tube, a liquid inlet tube, a gas exit tube through a reflux condenser, and a liquid exit tube, was charged with 8.0 g (0.060 mole) of lithium iodide, 1.4 g (0.020 mole) of lithium nitrate and 140 ml of acetic acid, and then pressurized to a pressure of 20 kg/cm² gauge with a gas mixture comprising by volume 88% of nitrogen, 4% of oxygen and 8% of ethylene. The reactor was heated gradually to 127°C with stirring and maintained at this temperature, while feeding the gas mixture into the reactor at a rate of 36 standard litres per hour. A solution of 1 ml of nitric acid dissolved in 20 ml of acetic acid was pumped into the reactor with the use of a micro-pump. After the addition of nitric acid, the reaction mixture was withdrawn from the reactor via the liquid exit pipe at a rate of 20 ml per hour, and an amount of nitric acid was added to the recovered reaction mixture to provide a volume ratio of nitric acid to the recovered reaction mixture of 1:20, and then the recovered reaction mixture containing nitric acid was recycled to the reactor with the use of a micro-pump at a rate of 21 ml per hour.

The reaction was carried out continuously under the above-described conditions, and steady-state was reached 2 hours after initiating the introduction of the gas mixture, and then the reaction was continued for an additional 5 hours, during which time average conversions of both ethylene and oxygen were 45%.

At the end of 7.5 hours from the time of initiating the introduction of the gas mixture, the addition of nitric acid was terminated, and then the conversions of ethylene and oxygen decreased suddenly and fell to about 0% in the subsequent 2 hours.

The total amounts of EGMA and EGDA formed in the 9.5 hours reaction period were 0.42 mole.

EXAMPLE 6

The reactor, as described in Example 5, was charged with 8.5 g (0.060 mole) of 1,2-diiodoethane, 1.4 g (0.020 mole) of lithium nitrate and 160 ml of acetic acid.

The reaction was carried out in the same manner as in Example 5, with the exception that a flow rate of the gas mixture was 15 standard litres per hour, and that nitric acid was not added to the recycled reaction mixture. The reaction occurred one hour after initiating the introduction of the gas mixture, at which time the conversions

per pass of ethylene and oxygen were 33% and 52% respectively. At the end of 3 hours from the time of initiating the introduction of the gas mixture, the conversions per pass of ethylene and oxygen were 74% and 83% respectively.

EXAMPLE 7

To a reactor similar to that described in Example 1 were added 3.3 g (20 millimoles) of potassium iodide, 1 ml (10 millimoles) of nitric acid, 0.5 g of activated carbon prepared from coconut shells (manufactured by Dai-ichi Carbon Industries Company) and 80 ml of acetic acid. The flask was set up in an oil bath maintained at 65°C. A gas mixture comprising by volume 8.5% of oxygen, 80% of nitrogen and 11.5% of ethylene was fed through the reaction mixture at a rate of 1.15 standard litres per hour with continuous stirring of the reaction mixture. At the conclusion of the one hour reaction period, the conversion of ethylene was 90%. The combined yields of EGDA and EGMA were 95% based on the reacted ethylene. Trace amounts of EDA and AcH were detected as by-products.

EXAMPLE 8

Employing 0.75 g (5 millimoles) of sodium iodide in place of potassium iodide, Example 7 was repeated. At the conclusion of the one hour reaction period, the conversion of ethylene was 80%, and the combined yields of EGDA and EGMA were 95% based on the reacted ethylene.

EXAMPLE 9

Employing 0.5 g of powdery graphite (manufactured by Kanto Chemical Company) in place of activated carbon, Example 7 was repeated. At the end of the one hour reaction period, the conversion of ethylene was 86% and the combined yields of EGDA and EGMA were 95% based on the reacted ethylene.

EXAMPLE 10

To a reactor similar to that described in Example 1 was added a solution of 155 mg (0.3 millimole) of chloroplatinic acid, 4 g (30 millimoles) of lithium iodide and 1.5 g (20 millimoles) of lithium nitrate in 80 ml of acetic acid. The flask was set up in an oil bath maintained at 80°C. A gas mixture comprising oxygen, nitrogen and ethylene was fed in the proportions by volume of 0.8 O₂/7.2 N₂/1.2 ethylene through the reaction mixture at a rate of 1.15 standard litres per hour with continuous stirring of the reaction mixture. At the end of the 2 hours reaction period, the conversion of ethylene was 80%, and the yields of EGMA and EGDA were 9.5 millimoles and 0.7 millimole respectively. The selectivity of the reacted ethylene to EGMA and EGDA was above 99%. Trace amounts of EDA and AcH were detected as by-products.

EXAMPLE 11

Employing 20 mg (0.038 millimole) of chloroplatinic acid, 4 g (30 millimoles) of lithium iodide and 0.75 g (10 millimoles) of lithium nitrate, Example 10 was repeated. The conversion of ethylene was not varied for 6 hours from the time of initiating the reaction and was 60%. The selectivity of the reacted ethylene to EGMA and EGDA was not varied for 6 hours from the time of initiating the reaction and was 99%. Trace amounts of AcH and EDA were obtained.

EXAMPLE 12

To a reactor similar to that described in Example 1 were added 0.5 g (0.05 millimole calculated as platinum metal) of a platinum catalyst supported on activated carbon having a platinum content of 0.5 weight percent (manufactured by Japan Engelhardt Company), 4 g (30 millimoles) of lithium iodide, 0.69 g (10 millimoles) of lithium nitrate and 80 ml of acetic acid. The reaction was carried out for 2 hours under the same conditions as in Example 10. The conversion of ethylene was 85%, and the selectivity of the reacted ethylene to EGMA and EGDA was 99%. Trace amounts of EDA and AcH were detected as by-products.

EXAMPLE 13

Employing 1 ml of concentrated nitric acid in place of lithium nitrate, Example 12 was repeated. At the end of the 2 hours reaction period, the conversion of ethylene was 70%, and the selectivity of the reacted ethylene to EGMA and EGDA was 99%.

EXAMPLE 14

Employing 3.3 g (20 millimoles) of potassium iodide and 1 ml of nitric acid in

place of lithium iodide and lithium nitrate respectively, Example 12 was repeated. At the end of the 2 hours reaction period, the conversion of ethylene was 70%, and the selectivity of the reacted ethylene to EGMA and EGDA was 99%. A trace amount of EDA was detected.

EXAMPLE 15

A titanium-lined autoclave was charged with 10 mg (0.02 millimole) of chloroplatinic acid, 1.3 g (10 millimoles) of lithium iodide, 0.14 g (2 millimoles) of lithium nitrate and 30 ml of acetic acid, and then pressured with 3 kg/cm² of ethylene and 30 kg/cm² of a gas mixture comprising by volume 4% of oxygen and 96% of nitrogen. The autoclave was heated to a temperature of 80°C with stirring, and the reaction was carried out for 2 hours. The yields of EGDA and EGMA were 2.10 millimoles and 2.30 millimoles respectively. A trace amount of EDA was detected.

EXAMPLE 16

A titanium-lined autoclave was charged with 0.20 g (0.020 millimole calculated as platinum metal) of a platinum catalyst the same as that used in Example 12, 1.7 g (10 millimoles) of potassium iodide, 0.14 g (2 millimoles) of lithium nitrate and 30 ml of acetic acid, and then pressured with ethylene and a gas mixture comprising oxygen and nitrogen in the same manner as in Example 15. The autoclave was heated to a temperature of 80°C, and the reaction was carried out for 2 hours. The yields of EGDA and EGMA were 3.38 millimoles and 3.48 millimoles respectively. A trace amount of EDA was detected.

EXAMPLE 17

Employing 0.14 g (2 millimoles) of sodium nitrate in place of lithium nitrate, Example 16 was repeated. The yields of EGMA and EGDA were 6.11 millimoles and 1.50 millimoles respectively.

EXAMPLE 18

To a reactor similar to that described in Example 1 were added 0.5 g (0.05 millimole calculated as platinum metal) of a platinum catalyst the same as that used in Example 12, 2.68 g (20 millimoles) of lithium iodide, 0.69 g (10 millimoles) of sodium nitrite and 80 ml of acetic acid. A gas mixture having the same composition as that used in Example 10 was passed through the reactor in the same manner as in Example 10. At the end of the 2 hours reaction period, the conversion of ethylene was 74%, and the selectivity of the reacted ethylene to EGMA and EGDA was 99%. A trace amount of EDA was detected as a by-product.

EXAMPLE 19

To a reactor similar to that described in Example 1 were added 0.2 g (0.02 millimole calculated as platinum metal) of a platinum catalyst the same as that used in Example 12, 1.3 g (10 millimoles) of lithium iodide, 0.69 g (10 millimoles) of lithium nitrate and 80 ml of acetic acid. The reactor was set up in an oil bath maintained at 80°C. A gas mixture comprising oxygen, nitrogen and propylene was fed in the proportions by volume of 0.8 O₂/7.2 N₂/1.2 propylene through the reaction mixture at a rate of 1.50 standard litres per hour with continuous stirring of the reaction mixture. At the end of the 2 hours reaction period, the conversion of propylene was 25%, and the selectivity of the reacted propylene to propylene glycol diacetate and propylene glycol monoacetate was above 99%. A trace amount of propylidene diacetate was detected as a by-product.

EXAMPLE 20

To a reactor similar to that described in Example 1 were added 2.0 g (15 millimoles) of lithium iodide, 1 ml (10 millimoles) of nitric acid, 1.8 g (10 millimoles) of vanadium pentoxide and 80 ml of acetic acid. The flask was set up in an oil bath maintained at 80°C. A gas mixture comprising by volume 80% of nitrogen, 8.5% of oxygen and 11.5% of ethylene was fed through the reaction mixture at a rate of 1.15 standard litres per hour with stirring of the reaction mixture. At the end of the one hour reaction period, the conversion of ethylene was 90%. Analysis showed the formation of EGDA, EGMA and IEA. The selectivity of the reacted ethylene to EGDA, EGMA and IEA was above 95%.

EXAMPLES 21—36

To a reactor similar to that described in Example 1 were added 2 g (15 millimoles) of lithium iodide or 3.3 g (20 millimoles) of potassium iodide as an iodine source, 1 ml (10 millimoles) of nitric acid as a nitrogen oxide, 80 ml of acetic acid and a promoter indicated in the following table. A gas mixture was passed through the reaction mixture in the same manner as in Example 20, while maintaining the reaction

temperature at 80°C. However, when the promoter was a nitrate, nitric acid was not added. At the conclusion of the one hour reaction period, the conversion of ethylene in each reaction was between 55 and 99%. The selectivity of the reacted ethylene to EGDA, EGMA and IEA was similar to that in Example 16. The results are summarized in the following table.

Example No.	Iodide	Promoter, Amount (g)	Conversion of Ethylene (after one hour)
21	LiI	TeO ₂ , 1.6 g	85%
22	KI	Silica-Alumina, 0.5	70
23	KI	Na ₂ TeO ₃ , 2.2	70
24	KI	Pb(OAC) ₄ , 4.3	70
25	KI	MoO ₃ , 1.5	55
26	KI	H ₂ WO ₄ , 2.5	70
27	KI	Iron powder, 0.55	80
28	KI	HAuCl ₄ · 4H ₂ O, 0.13	56
29	KI	FeCl ₃ , 1.6	88
30	KI	Ni(NO ₃) ₂ · 6H ₂ O, 2.9	74
31	KI	Co(NO ₃) ₂ · 6H ₂ O, 2.9	90
32	KI	ZnO, 0.8	63
33	KI	CuO, 0.8	80
34	KI	Bi(NO ₃) ₃ · 5H ₂ O, 4.9	55
35	KI	B ₂ O ₃ , 0.7	99
36	KI	ZrOCl ₂ · 8H ₂ O, 3.2	92

REFERENCE EXAMPLE 1

To a reaction flask the same as that described in Example 1 were added 4 g (30 millimoles) of lithium iodide and 80 ml of acetic acid. The reaction was carried out under the same conditions as those of Example 1. At the conclusion of the one hour reaction period, the conversion of ethylene was 1%.

REFERENCE EXAMPLE 2

To a reaction flask the same as that described in Example 1 were added 0.69 g (10 millimoles) of lithium iodide and 80 ml of acetic acid. The reaction was carried out under the same conditions as those of Example 1.

At the conclusion of the one hour reaction period, the conversion of ethylene was less than 1%.

REFERENCE EXAMPLE 3

Example 12 was repeated except that lithium nitrate was not added. At the end of the 2 hours reaction period, the conversion of ethylene was 3%, and the selectivity of the reacted ethylene to EGMA and EGDA was 95%.

REFERENCE EXAMPLE 4

To a reactor the same as that described in Example 1 were added 130 mg (0.25 millimole) of chloroplatinic acid, 4 g (30 millimoles) of lithium iodide and 80 ml of acetic acid saturated with iodine.

A gas mixture was passed through the reaction mixture in the same manner as in Example 1. At the end of the 2 hours reaction period, the conversion of ethylene was 4%, and the selectivity of the reacted ethylene to EGMA and EGDA was 99%.

REFERENCE EXAMPLE 5

A titanium-lined autoclave was charged with 0.2 g (0.02 millimole calculated as platinum metal) of a platinum catalyst the same as that used in Example 12, 1.3 g (10 millimoles) of lithium iodide and 30 ml of acetic acid, and then pressurised with 3 kg/cm² of ethylene and 30 kg/cm² of a gas mixture comprising by volume 4% of oxygen and 96% of nitrogen. The autoclave was heated to a temperature of 170°C with stirring and the reaction was carried out for 2 hours. The yields of EGDA and EGMA were 0.45 millimole and 0.13 millimole respectively.

REFERENCE EXAMPLE 6

Example 12 was repeated except that lithium iodide and lithium nitrate were not added. The conversion of ethylene was less than 1%. The addition of 0.69 g (10 millimoles) of lithium nitrate to the system did not vary the conversion to a significant extent.

REFERENCE EXAMPLE 7

Example 11 was repeated except that lithium nitrate and lithium iodide were not added. The conversion of ethylene was less than 1%. The addition of 0.69 g (10 millimoles) of lithium nitrate to the system did not vary the conversion to a significant extent.

REFERENCE EXAMPLE 8

Employing 1.66 g (10 millimoles) of potassium iodide, 2.45 g (10 millimoles) of Mn(CH₃CO₂)₂·4H₂O and 80 ml of acetic acid, Example 3 was repeated. At the end of the one hours reaction period, the conversions per pass of both ethylene and oxygen were less than 1%. The addition of 1.27 g (5 millimoles) of iodine to the system did not increase the conversions of ethylene and oxygen.

REFERENCE EXAMPLE 9

Employing 1.66 g (10 millimoles) of potassium iodide, 2.32 g (10 millimoles) of Fe(CH₃CO₂)₃ and 80 ml of acetic acid, Example 3 was repeated. At the end of the one hour reaction period, the conversions per pass of both ethylene and oxygen were less than 1%. The addition of 1.27 g (5 millimoles) of iodine did not increase the conversions of ethylene and oxygen.

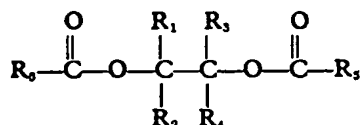
REFERENCE EXAMPLE 10

Employing 2.54 g (10 millimols) of iodine, 7.9 g (100 millimoles) of pyridine and 80 ml of acetic acid, Example 3 was repeated. At the end of the one hour reaction period, the conversions per pass of both ethylene and oxygen were less than 1%.

It can be seen from the comparison of the examples with the reference examples that the combination of iodine or iodine-containing compound and the nitrogen oxide or nitrogen oxide-containing compound increases the yields of the acetates of ethylene glycol considerably as compared to the use of the iodine or iodine-containing compound or the nitrogen oxide or nitrogen oxide-containing compound alone.

WHAT WE CLAIM IS:—

1. A process for the production of an alkylene glycol ester having the general formula (I):



wherein R₁, R₂, R₃ and R₄ are selected from hydrogen, C₁—C₂₀ alkyl and C₆—C₂₀

aryl, and R_5 is C_1-C_{20} alkyl or C_6-C_{20} aryl, and/or an alkylene glycol ester having the general formula (II):



wherein R_1 , R_2 , R_3 , R_4 and R_5 are as defined herein above, any of the above-mentioned alkyl and aryl groups being optionally substituted, which comprises reacting in a liquid phase an olefine having the general formula (III):



wherein R_1 , R_2 , R_3 and R_4 are as defined herein above, a carboxylic acid having the formula (IV):



wherein R_5 is as defined herein above, and molecular oxygen or other oxidising agent, in the presence of iodine or an iodine-containing compound which can reversibly vary its oxidation number and a nitrogen oxide or a compound containing a nitrogen oxide which can vary its oxidation number as catalyst.

2. The process claimed in Claim 1, wherein R_1 , R_2 , R_3 and R_4 are selected from hydrogen, C_1-C_{10} alkyl and C_6-C_{10} aryl, and R_5 is C_1-C_{10} alkyl or C_6-C_{10} aryl.

3. The process claimed in Claim 1 or Claim 2, wherein the olefine is ethylene or propylene, and the carboxylic acid is acetic acid.

4. The process claimed in any preceding claim, wherein the iodine-containing compound is selected from hydroiodic acid and salts thereof, hypoiodous acid and salts thereof, periodic acid and salts thereof, iodine-containing complexes, and organic iodine compounds capable of liberating iodide ion by solvolysis under the reaction conditions.

5. The process claimed in any preceding claim, wherein the amount of the iodine or iodine-containing compound used is up to one equivalent per litre of the reaction solution.

6. The process claimed in any preceding claim, wherein the nitrogen oxide or compound containing nitrogen oxide is selected from nitric acid and salts thereof, nitrous acid and salts thereof NO , NO_2 , N_2O_3 , N_2O_4 and N_2O_5 .

7. The process claimed in any preceding claim, wherein the amount of the nitrogen oxide or compound containing nitrogen oxide used is up to one mole (calculated as nitrogen oxide) per litre of the reaction liquid.

8. The process claimed in any preceding claim, wherein there is also present a promoter selected from carbon and elements selected from lithium, beryllium, boron, sodium, magnesium, aluminium, silicon, potassium, calcium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, germanium, gallium, zirconium, niobium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, antimony, tellurium, barium, cerium, hafnium, tantalum, tungsten, rhenium, osmium, iridium, platinum, gold, mercury, thallium, lead and bismuth, and compounds containing any of the said elements.

9. The process claimed in Claim 8, wherein the promoter is selected from carbon and elements selected from lithium, boron, sodium, aluminium, silicon, potassium, vanadium, iron, cobalt, nickel, copper, zinc, zirconium, molybdenum, tellurium, tungsten, platinum, gold, lead and bismuth, and compounds containing any of the said elements.

10. The process claimed in Claim 9, wherein the promoter is selected from carbon and elements selected from boron, iron, cobalt, nickel, zirconium and platinum, and compounds containing any of the said elements.

11. The process claimed in any preceding claim, wherein the reaction temperature is in a range of from room temperature to 200°C .

12. The process according to Claim 1 for the production of acetates of ethylene glycol.

13. The process according to Claim 1 for the production of acetates of propylene glycol.

14. The process according to Claim 1 substantially as herein described with particular reference to any one of Examples 1 to 36.

15. An alkylene glycol ester or mixture of alkylene glycol esters which has been obtained by the process claimed in any preceding claim.

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